Electrochromic Polymer Devices:  
Active-Matrix Displays and Switchable Polarizers

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Dept. of Science and Technology
Linköping University
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Abstract

Major efforts have been spent during recent years in worldwide attempts to achieve an electronic paper technology; the common name for novel flexible displays utilizing substrates such as paper, plastics or thin metal sheets. Various kinds of technology are available that potentially will be used for an electronic paper, which differs from each other mainly with respect to the choice of active materials, substrates and manufacturing techniques. There are many applications for electronic paper technology, ranging from high-resolution displays used in electronic books to updateable large-area billboards. The latter suggests a novel electronic display function that could extend the utilization of cellulose-based paper, which is one of the most common materials ever produced by mankind, by using the paper as a thin and flexible carrier. The requirement for fast update speed in such large area applications would probably be a bit more relaxed compared to traditional display technologies, while low-power consumption and bi-stability are among the factors that should be further emphasized, together with the utilization of well-established printing techniques to enable low-cost manufacturing of the displays. The choice of active materials is therefore crucial in order to reach these objectives in reality and this paves the way for printable conjugated polymers with electrochromic properties. Chemical synthesis of these materials during the last decades has resulted in a vast variety of electrochromic polymers with custom-tailored functionality covering a broad range of optical absorption and electrical conductivities.

This thesis review the studies done on the electrochemical switching of poly(3,4-ethylenedioxythiophene) (PEDOT). For this material both the electrical conductivity and the optical absorption is controlled by the oxidation state. Active matrix addressed displays that are printed on flexible substrates have been obtained by arranging electrochemical smart pixels, based on the combination of electrochemical transistors and electrochromic display cells, into cross-point matrices. The resulting polymer-based active-matrix displays are operated at low voltages and the same active material can be used in electrochemical transistors and conducting lines and in electrochromic display cells employing the electronic and the opto-electronic properties of the material, respectively. In addition to this, a switchable optical polarizer is briefly discussed. This is a device utilizing electrochromism of stretch-aligned polyaniline (PANI). The combination of two identical devices in a vertical architecture, orthogonally oriented with respect to each other, results in a filter in which the orientation of the polarized optical absorption is governed by the voltage polarity applied to the device.
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Papers included in the thesis

Paper 1

Active Matrix Displays Based on All-Organic Electrochemical Smart Pixels Printed on Paper
*Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren*
Author’s contribution: More than half of the experimental work. Wrote parts of the first draft of the manuscript and was involved in the final editing until manuscript submission.

Paper 2

Organic Electrochemical Smart Pixels
*Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren*
Author’s contribution: All experimental work, wrote most of the manuscript.

Paper 3

Switchable Optical Polarizer Based on Electrochromism in Stretch-Aligned Polyaniline
*Peter Andersson, Thomas Kugler and Magnus Berggren*
Author’s contribution: All experimental work. Wrote the first draft of the manuscript and was involved in an iterative editing process until manuscript submission.
## Contents

1. **INTRODUCTION TO ORGANIC ELECTRONICS**  
   1

2. **CONJUGATED POLYMERS**  
   5
   2.1 **INTRODUCTION TO CONJUGATED POLYMERS**  
      5
      2.1.1 **HYBRIDIZATION**  
         6
      2.1.2 **σ-Bonds**  
         7
      2.1.3 **π-Bonds**  
         7
   2.2 **WELDING OF ACETYLENE INTO CONJUGATED POLYACETYLENE**  
      9
   2.3 **POLYMER BAND GAP ENERGY**  
      9
   2.4 **CREATION OF CHARGE CARRIERS THROUGH POLYMER DOPING**  
      10
      2.4.1 **SOLITONS**  
         11
      2.4.2 **POLARONS**  
         13
   2.5 **EXAMPLES OF CONJUGATED POLYMER SYSTEMS**  
      14

3. **ELECTROCHEMICAL DEVICES BASED ON PEDOT:PSS**  
   17
   3.1 **ELECTROCHROMISM IN PEDOT:PSS**  
      19
   3.2 **THE ELECTROCHROMIC DISPLAY CELL**  
      20
   3.3 **THE ELECTROCHEMICAL TRANSISTOR**  
      23
      3.3.1 **THREE-TERMINAL ELECTROCHEMICAL TRANSISTOR DEVICE**  
         23
      3.3.2 **FOUR-TERMINAL ELECTROCHEMICAL TRANSISTOR DEVICE**  
         25
   3.4 **ELECTROCHEMICAL SMART PIXELS**  
      26
   3.5 **THREE- OR FOUR-TERMINAL TRANSISTORS IN THE SMART PIXELS**  
      27
   3.6 **ELECTROLYTE DEPENDENCE**  
      28

4. **ACTIVE MATRIX ADDRESSED DISPLAYS**  
   31

5. **OPTICAL POLARIZER BASED ON ELECTROCHROMIC SWITCHING IN STRETCH-ALIGNED POLYANILINE**  
   41

6. **CONCLUSIONS AND OUTLOOK FOR THE FUTURE**  
   43

7. **REFERENCES**  
   45

**PAPER 1**  
49

**PAPER 2**  
51

**PAPER 3**  
53
1 Introduction to organic electronics

The steadily increasing desire for faster, smaller and cheaper electronic products in our society has not only encouraged the traditional inorganic semiconductor manufacturing facilities to invent and put novel electronic devices into the market, but also forced them to allocate time and financial resources on research and development to meet both customer demand and to respond to competition in between industries; the continuous strive to achieve a more efficient manufacturing process. The performance of advanced microprocessors and memories is still improving according to the famous exponential law predicted by Gordon Moore, that is, that the number of transistors placed on a chip would double in either every year (1965) or every two years (1975) [1]. However, as the feature size has become smaller than the wavelength of visible light, typically 65 nanometers in frontier technologies, limitations regarding optical lithography patterning and larger leakage currents in the transistors are looming. The International Technology Roadmap for Semiconductors [2] has predicted that the information technology miniaturization will continue for another few years (2010) before the optical lithography patterning method utilized today needs to be replaced.

From this, and also through progress in materials science research during recent decades, the organic electronics research field has been brought to light. Examples of applications for organic materials range from high-end memory devices to low-end printable displays. The common thread in these devices is that carbon nanotubes, switchable organic molecules or conducting polymers are the active materials, where the latter is the focus of this thesis.

Polymers have traditionally been used in electrical applications as the insulating material that surround metal wires in order to prevent short-circuits between conductors, primarily because most polymers are electrically insulating. However, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa changed this point of view nearly three decades ago when they observed a tremendous conductivity increase, by a factor more than one billion, upon chemical oxidation of a polymer known as polyacetylene [3]. Polymer-based organic electronics has evolved into a well-established research field since then and further attention was attracted to the field in the year 2000 when these three scientists were awarded the Nobel Prize in Chemistry “for the discovery and development of conductive polymers” [4].
There is a seemingly endless number of polymeric materials today, either synthesized by mankind or produced by nature. Despite a broad spectrum of chemical formulas and material properties possessed by various polymers, they are all built-up of from monomeric units coupled to each other to form long macromolecular chains upon polymerization. The result is an amorphous material that often can be processed from solution into very thin and flexible films by using spin-coating or printing techniques. The ability to process the polymers from solution is a key factor in manufacturing flexible electronic devices at low cost. Another important feature of polymers is that their optical and electronic properties can be tuned via chemical synthesis and material design, which allows for novel materials containing tailor-made functionalities.

Various organic electronics device concepts have been developed from conjugated polymers. Examples previously reported in literature are light emitting diodes [5], light-emitting electrochemical cells [6], solar cells [7], field-effect transistors [8], lasers [9] and transistor circuits manufactured with printing techniques [10].

Furthermore, most electrically conductive polymers respond to electrochemical switching, a process which can be used to translate signals between electronic and ionic [11]. Optical, electrical, volumetric and surface energy properties of the polymers depend on the electrochemical state of the polymer, that is, oxidation or reduction, and these effects can be used in various electrochemical devices through reversible electrochemical switching. A change in optical absorption due to electrochemistry, also denoted electrochromism, has been reported in smart windows [12] and display cells [13]. A change in electrical conductivity can be achieved from the doping or de-doping process upon oxidation or reduction and this effect can be used to modulate the current through electrochemical diodes [14] and electrochemical transistors [15, 16]. A volumetric change occurs when the mobile ions enter or escape the polymer upon electrochemical switching, an effect which can be used in electroactuators for different kinds of micro-robotic systems [17]. The surface energy change is caused either by ion motion or polarization in the film and is dependent on the oxidation state of the polymer, an effect that can be used in micro-fluidics to control the motion of liquids [18].

The main focus in this thesis is electronic and optical changes based on electrochemical switching in conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI), and how they can be utilized in novel organic electronic devices that
operate at low voltages, typically below 2V. An electrochemical smart pixel can be achieved through the combination of an electrochemical transistor and an electrochromic display cell, which use the change in electrical conductivity and optical absorption in PEDOT, respectively. Integrating such smart pixels at each intersection in cross-point matrices opens up the possibility to realize actively addressed matrix displays, manufactured by printing techniques, on flexible substrates. Furthermore, in a project that slightly deviates from active matrix addressed displays, a switchable optical polarizer based on electrochromism in stretch-aligned PANI will be briefly discussed. Orthogonal switching of the polarized optical absorption can be achieved in this device; an effect that originates from the voltage polarity that is applied to the electrochromic films in the device.
2 Conjugated polymers

2.1 Introduction to conjugated polymers

As previously mentioned, Heeger, MacDiarmid and Shirakawa were awarded the Nobel Prize in chemistry a few years ago for the discovery of conducting polymers [4]. Their initial observation was that exposing oxidative iodine vapor to intrinsically insulating polyacetylene resulted in more than a billion-folded increase of the electrical conductivity in the polymer [3]. The terms oxidation and reduction can refer to p-doping and n-doping of a polymer, respectively, and the change in conductivity is analogous to the impact of doping in silicon or other inorganic semiconductors.

Nearly all polymers contain a backbone chain of carbon atoms. The electrical conductivity of a polymeric material, ranging from insulating via semiconducting to conducting, depends on the electronic states formed of the carbon atoms along the polymer and how these interact with each other. In addition, the charge conductivity depends on morphology, the overall chemical nature of the polymer and the attached substituents coupled to the polymer backbone. In order to provide understanding of the electronic structure and the bonding configuration in conjugated polymers, a brief description of the electronic structure of an isolated carbon atom and a dihydrogen molecule is given below.

The Pauli exclusion principle suggests that no two electrons of identical spin may be in the same individual state. In an isolated atom, this implies that the electrons are separated into different atomic orbitals defining regions in space with high probability of finding an electron [19]. There are six electrons in a carbon atom; two of them tightly surround the nucleus in the 1s orbital, while the other four are valence electrons in the 2s and 2p orbitals, see Figure 1a. It is the valence electrons in carbon atoms that allow the formation of a molecule since their electron densities are farther away from the nucleus than the core (1s) electrons are.

The notion of covalent bonding can be simply illustrated with the dihydrogen molecule, where each hydrogen atom carries one electron in a 1s atomic orbital. These two electrons sense the positive charges of the nuclei when the two hydrogen atoms are in proximity of each other, and two wave functions, denoted bonding and antibonding molecular orbitals, can be used to describe how the electrons travel around the nuclei. The molecule reaches its lowest
total energy if the two electrons are represented with the bonding molecular orbital, in which the two electrons have opposite spin. The occupation of a molecular bonding orbital defines a covalent bond, while the occupation of an antibonding orbital would destabilize the molecule, see Figure 1b.

Figure 1. a) A sketch that shows the electronic configuration of the carbon atom ground state. b) The formation of a covalent bond in the dihydrogen molecule.

2.1.1 Hybridization

When two carbon atoms are brought together to form a molecule, they form hybrid orbitals due to the new potential created by the surrounding atoms. Such hybrid orbitals can be described from a linear combination of the atomic orbitals. One s-orbital and three p-orbitals of the tetravalent carbon atom can be combined to form a new set of four sp³-hybridized orbitals. Following the same principle as described previously for the dihydrogen molecule, the singly occupied hybrid orbitals of carbon allow the formation of methane, CH₄, with four equivalent bonds to hydrogen atoms. This corresponds to four bonds that are oriented in a tetrahedral structure with an angle separation of 109.5° with respect to each other. Furthermore, both sp²- and sp-hybridized orbitals can be formed. For carbon atoms in a conjugated molecule, a mixture of one s-orbital and two p-orbitals can be combined to form three sp²-hybrid orbitals. This new set of hybrid orbitals hold three bonds that are triagonally arranged in the same plane as the nucleus with a separation angle of 120°. The last possible hybridization state is obtained by the combination of one s-orbital and one p-orbital, which results in two sp-hybridized orbitals that are represented by two bonds oriented to opposite one another.
2.1.2 σ-Bonds

The hydrocarbon molecule ethane, C\textsubscript{2}H\textsubscript{6}, consists of two sp\textsuperscript{3}-hybridized carbon atoms and six hydrogen atoms, where the latter consist of only 1s-orbitals since they have only one valence electron. The bond between a carbon atom and a hydrogen atom is formed by an overlap between the sp\textsuperscript{3}-orbital of carbon and the 1s-orbital of hydrogen and the bond between the two carbon atoms arises from an overlap of two sp\textsuperscript{3}-orbitals. The overlaps in the ethane molecule create seven sigma (σ) bonds that are each circularly symmetrical along the bond axis. Repeating ethane molecular units results in a polymer chain known as polyethylene (C\textsubscript{2}H\textsubscript{4})\textsubscript{n}; a flexible material widely used in, for example, plastic bags. Since all valence electrons are occupied and localized in σ-bonds in polyethylene, this polymer shows a purely insulating electronic property.

2.1.3 π-Bonds

The hydrocarbon molecule ethene, C\textsubscript{2}H\textsubscript{4}, consists of four hydrogen atoms and two sp\textsuperscript{2}-hybridized carbon atoms that share two valence electron pairs in a double bond, which results in a total of six σ-bonds. Two valence electrons are, therefore, not yet involved in the molecular formation, that is, one valence electron per carbon atom remains in the 2p-orbital. Instead of taking part in σ-bond formation, the remaining 2p-orbitals overlap above and below the nodal plane of the σ-double bond, orthogonal to the σ-bond bond axis, as they form another type of covalent molecular interaction denoted as a pi (π) bond. Repeating ethene molecular units result in the semi-conducting polyacetylene (C\textsubscript{2}H\textsubscript{2})\textsubscript{n}. Electrons that are involved in π-bonds are desired in semiconducting polymers since they are delocalized at higher energies than localized σ-bond electrons and can be moved more easily along a macromolecular chain in the vicinity of an applied electric field.

In summary, the localized electrons in the σ-bonds form the backbone in a polymer chain and dominate the mechanical properties, while the electrons in the π-bonds are delocalized along the chain and responsible for the electrical and optical properties of a conjugated polymer material. The σ-bonds form completely filled low-lying energy bands that have a larger energy gap (the energy between bonding and antibonding states) than the π-electrons, see Figure 2.
Figure 2. Relative energies of molecular orbitals are shown [19]. The star (*) denotes an antibonding molecular orbital. $\sigma$-electrons require a relatively high excitation energy and correspond to the glue that holds the atoms together in the molecule, while $\pi$-electrons are easier to excite and therefore define the optical and electronic properties of the molecule.
2.2 Welding of acetylene into conjugated polyacetylene

The key to electrical conductivity in a polymer is to achieve conjugation in the polymer backbone, or in other words, an alternation between single and double bonds along the carbon atoms in the polymer chain. Conjugated bonds define an unsaturated polymer system that contains $\pi$-electrons available for charge transport, in comparison with a saturated polymer chain where the carbon atoms are attached to neighboring carbons by single $\sigma$-bonds and the remaining valence electrons bind to other elements that are not participating in the polymer backbone. No charge transport will occur in the latter case since all the valence electrons are occupied in $\sigma$-bonds. The monomeric units that build up polyacetylene are connected to each other with single bonds. This results in the conjugated polymer chain shown in Figure 3, in which the non-hybridized valence electron in each carbon atom forms the delocalized $\pi$-bond from a neighboring overlap that is orthogonally oriented to the plane of the $\sigma$-bonding sp$^2$-orbitals.

![Figure 3](image)

Figure 3. The conjugated bonds in polyacetylene are shown, that is, an alternation of single and double bonds along the polymer backbone.

2.3 Polymer band gap energy

The band gap energy in an undoped organic semiconductor is typically between 2 and 4eV and the Fermi energy level in an intrinsic semiconductor is positioned in the middle of the band gap. Semiconducting materials have a similar structure compared to insulators at very low temperatures, that is to say that the highest occupied molecular orbital (HOMO) energy level (in the molecular picture), i.e. the top of the filled valence band (in the solid-state picture), is distinctly separated from the lowest unoccupied molecular orbital (LUMO) energy level, i.e. the bottom of the conduction band, by a band gap with no allowed energy states, see Figure 4. Electrons can be thermally excited to the LUMO energy level when the temperature is increased, even though this is considered negligible in most organic semiconductors due to their relatively high band gaps compared to inorganic semiconductors.
The difference in band gap energies in semiconductors and insulators, as well as the absence of a forbidden energy gap in conductors, are shown. The Fermi energy levels are positioned in the middle of the respective band gaps under the assumptions of low temperature and neutral materials without dopant species.

The exact band gap in a polymer film is not easily determined. A polymer film consists of many chains, and the energy gap can vary between these individual chains due to different factors such as defects and varying polymer chain length. Thus, determination of the macroscopic band gap value for a polymer film is an average value derived from the energy gaps of many polymer chains. The conductivity in a polymer increases if the temperature is elevated, which is mainly due to enhanced hopping probability between available localized sites along the polymer chains. This is contrary to the behavior observed in metals, in which the higher degree of phonons at higher temperatures reduces the electrical conductivity by scattering of delocalized charge carriers.

### 2.4 Creation of charge carriers through polymer doping

Conjugated polymers are typical semiconductors in their pristine form, a character that is utilized in electronic and opto-electronic devices. In their doped form, they can reach conductivity values that are approaching those of true metals. Based on this, these systems are therefore often denoted as one-dimensional synthetic metals due to the polymer chain structure. Figure 5 shows the conductivity values in various materials.
Figure 5. The conductivity for various materials is shown [4]. Conjugated polymers can range from insulating to conducting, via the semiconducting state. A conductivity of $10^5$ S/m has for instance been reached in doped polyacetylene [20].

From the neutral state, conjugated polymers can be either p-doped or n-doped through an oxidation or reduction process, respectively. Oxidative doping is much more common in polymers since unstable alkali metals (Li, Na, K) have to be used in a reductive doping process, an inconvenience that requires an inert environment. Even if an n-doped polymer has been obtained, e.g. in vacuum, a spontaneous transition towards the neutral state occurs via oxidation if exposed to ambient atmosphere. In oxidative doping, an electron is removed from the HOMO energy level of the polymer chain, that thereby becomes positively charged (stabilized locally by an anion), and such charges are then able to create electrical current by migration in the polymer film. The opposite process occurs in reductive doping; an electron is added to the LUMO energy level of the polymer chain instead of being removed from the HOMO energy level.

### 2.4.1 Solitons

The structure of polyacetylene can be represented by either trans- or cis-isomerism, as shown in Figure 6. The energy in a degenerate system is said to be independent of the bond alternation, which is the case in trans-polyacetylene. In contrast, the change in bond length alternation is accompanied by a destabilization of the cis-polyacetylene chain, which is denoted as a non-degenerate ground state polymer. Trans-polyacetylene is more stable than cis-polyacetylene, even though neither isomeric state is stable enough in ambient environment to be interesting from an application point of view.
Figure 6. Shorthand notations of four different isomers of polyacetylene: (I) and (II) are the two degenerate isomers in trans-polyacetylene that have the same energy. (III) and (IV) are the high and low energy states of the non-degenerate cis-polyacetylene, respectively.

In trans-polyacetylene, i.e. for a degenerate ground state polymer, neutral defects, denoted solitons, can be formed on the polymer chains. A soliton is a domain wall that separates two regions characterized with different bond length alternation, and this defect is delocalized over a few neighboring monomers, as shown in Figure 7a. The electron associated with the soliton has its energy level in the middle of the gap of the trans-polyacetylene polymer chain. Since the energy of the polymer chain remains the same upon changing the bond length alternation in degenerate ground state polymers, the soliton appears as a mobile carrier. Doping of this polymer chain forces the neutral soliton into a charged but spin-less state, where either oxidative or reductive doping corresponds to a positively or negatively charged soliton, respectively, see Figure 7b.
2.4.2 Polarons

Inorganic semiconductors can be grown into a crystalline structure. Withdrawing an electron from such a structure results in a positive charge delocalized among many atoms within the crystal. The missing electron is, therefore, hardly noticed due to the strong delocalization effect. However, this will not be the case in polymeric materials since they are confined quasi-one-dimensional electronic systems with an amorphous structure. Withdrawal of an electron from a polymer, i.e. injection of a hole to the polymer, breaks the $\pi$-bond at the location where the electron was removed. The addition of charge is accompanied by a structure modification delocalized over a few monomers, and this charge defect, denoted a polaron, affects the bond length alternation compared to the rest of the neutral polymer chain.

Polarons can transport charge through the conjugated polymer, either along one polymer chain or, by hopping, between two chains, denoted intra- and inter-chain transport, respectively. To transport charges, a polaron must also break bonds as it travels; a polaron can therefore be seen as a package of delocalized charge that successively interchanges the conjugated bond configuration while it moves in the vicinity of charge neutralizing dopant counter ions. Oxidative doping of the non-degenerate conjugated system poly($para$-phenylene vinylene) (PPV) is shown in Figure 8a. The lowest energy of this macromolecular chain is found in the aromatic ground state. Withdrawal of one electron from this neutral state creates a positively charged polaron, i.e. a radical cation, and further oxidation may form a doubly charged bi-polaron in the excited quinoid energy state of the chain. Polarons can exist in four
different states, that is, positively charged polaron/bi-polaron and negatively charged polaron/bi-polaron, as shown in Figure 8b.

Figure 8. a) Oxidation of the aromatic ground state of a PPV-chain forms a charged polaron. Further oxidation results in the formation of a doubly charged bi-polaron in the excited quinoid state. Polaron and bi-polaron are responsible for the charge transport in conjugated polymer systems. b) Positive polarons and bi-polaron are obtained from oxidative doping, while the negative counterparts are resulting from a reductive doping process in which the conjugated polymer chain gains electrons.

2.5 Examples of conjugated polymer systems

Specific electronic and optical properties of conjugated polymers can be obtained at a molecular level during polymer synthesis, which is often scalable to higher volume for low-cost manufacturing of electronic devices. Several conjugated polymer families, all showing different properties, are available on the market. A few examples are mentioned below. Polypyrrole – Conjugated polymer that undergoes a volumetric change upon electrochemical switching. Based on this property, it is used as an artificial muscle in biological and micro-robotic systems [17].

Figure 9. The chemical structure of polypyrrole is shown.
Polythiophene – A conjugated polymer family with a lot of derivatives that are utilized in organic field effect transistors and polymer diodes [8].

Figure 10. The chemical structure of polythiophene is shown.

Poly(para-phenylene vinylene) – Another conjugated polymer family that is typically used in electroluminescent devices [5].

Figure 11. The chemical structure of poly(para-phenylene vinylene) is shown.

Polyaniline – Conducting polymer where both the electrical conductivity and the optical absorption can be electrochemically switched. This polymer was utilized to obtain the switchable optical polarizer presented in Paper 3 enclosed at the end of this thesis. It is manufactured in very large quantities, which promises low-cost production of organic electronic devices based on this material.

Figure 12. The chemical structures of the different oxidation states in polyaniline are shown. When the oxidation state, denoted y in the figure, equals 1, 0.5 or 0, the polymer is in its fully reduced leucoemeraldine state, intermediate emeraldine state or the fully oxidized pernigraniline state, respectively [21].
Poly(3,4-ethylenedioxythiophene) blended with the counter ion poly(styrene sulfonate), abbreviated PEDOT:PSS – This polythiophene derivative is one of the most commonly used, and also of crucial importance in this thesis since it is the active material in the electrochemical transistors, the electrochromic display cells and the conducting lines that are required in the active matrix addressed displays and the electrochemical smart pixels presented in Paper 1 and Paper 2 that are enclosed in the end of the thesis.

Figure 13. The chemical structures of poly(3,4-ethylenedioxythiophene) (PEDOT) and the common counter ion poly(styrene sulfonate) (PSS) are shown.
3 Electrochemical devices based on PEDOT:PSS

Major efforts have been spent during recent years in worldwide attempts to achieve an electronic paper technology — the common name for novel flexible displays utilizing substrates such as paper, plastics or thin metal sheets. There are, however, various kinds of technology available to obtain electronic papers with respect to the choice of active materials, substrates and manufacturing techniques. Examples include microencapsulated electrophoretic fluids [22, 23], Gyricon beads [24] and liquid crystals [23, 25, 26]. Applications for the electronic paper technology range from high-resolution displays for use in electronic books to updateable billboards. The latter is an example where novel display functions can potentially extend the utilization of cellulose-based paper, which is one of the most common materials ever produced by mankind, by using paper as a thin and flexible carrier. The requirements in this type of electronic paper display are not the same as in traditional systems, i.e. liquid crystal displays etc.; updating speed becomes less important while factors such as low-power consumption and bi-stability are further emphasized. Another powerful advantage of using paper, or other flexible substrates, is that it can be used in well-established printing techniques, which will allow low-cost manufacturing of devices. This, of course, requires that the active materials are printable. Thus, printable conjugated polymers possessing electrochromic properties are key to this research. Chemical synthesis of these materials during the last decades has resulted in a vast variety of electrochromic polymers with custom-tailored functionalities covering a broad range of optical absorption characteristics and electrical conductivities. PEDOT:PSS, poly(3,4-ethylenedioxythiophene) doped with the counter anion poly(styrene sulfonate), is one of the most commonly used polymers due to its stability and ease of manufacture. Large-scale manufacturing of this polymer/water emulsion provides for low-cost applications manufactured from spin-casting or printing techniques. PEDOT:PSS shows on stability in ambient atmosphere as well as high conductivity and smooth work function, which makes it suitable as a protective coating against electrostatic discharge on photographic films [27] and as a hole-injection electrode in solid-state organic light emitting devices [28], respectively.

Furthermore, electrochemical switching of PEDOT:PSS brings a two-folded effect where both the electrical conductivity and the optical absorption characteristics are dependent on the oxidation state of the material. Electrochemical transistors [16] and electrochemical logic circuits [29] have been presented in the past, as have the combination of electrochemical
transistors and electrochromic display cells arranged as smart pixels into active matrix addressed displays printed on ordinary cellulose-based paper. The latter has attracted attention of popular science [30, 31] and is further discussed in Paper 1. These polymer-based devices controlled by electrochemical switching are operated at low voltages and do not require critical dimensions to be patterned, unlike field-effect driven devices. Another advantage is that the very same active material (PEDOT:PSS) is used in the whole circuit, that is, in electrochemical transistors, electrochromic display cells and conducting lines, which promises easy manufacturing of all-organic and flexible active matrix addressed displays by printing techniques.

PEDOT is, in its pristine form, a semiconducting conjugated polymer with a rather low band gap below 2eV. The doped form of PEDOT, with for example PSS as the counter ion, is partly oxidized from the beginning and conducts current, which gives rise to an infinitely small band gap. The degree of doping that is required to make conjugated polymers conductive is typically very high, often reaching several tens on the percentage scale, compared with inorganic semiconductors that normally utilize doping fractions in the order of a few parts per million.

Oxidation of a PEDOT polymer chain is shown in Figure 14. Two electrons are withdrawn from the initially neutral PEDOT chain and a bi-polaron that carries a positive double charge is created. A large number of these charge carriers will form bi-polaronic bands within the band gap that allow for new optical transitions as well as an increased number of hopping sites, enhancing charge transport. The immobile anion PSS\(^{-}\) balances the charge of the oxidized form of PEDOT, while PSS\(^{+}\) binds to a mobile cation, typically provided from an external electrolyte, upon reduction of PEDOT.
Figure 14. The upper part of the figure is the PSS chain and the lower part is the PEDOT polymer chain in the form of a bi-polaron that is carrying a positive double charge. Negatively charged ions ensure the overall charge neutrality of the doped system and bi-polarons are responsible for the charge transport.

3.1 Electrochromism in PEDOT:PSS

PEDOT:PSS belongs to the class of materials dubbed electrochromic because it visibly changes color when oxidized or reduced. This opto-electronic property can be used to create display cells that are switchable between two different color states. The PEDOT:PSS that is utilized in most of the electrochemical devices reported here was provided by AGFA-Gevaert in Belgium under the trademark Orgacon EL-350 [32], which is a 200nm thick semi-oxidized layer of conducting PEDOT:PSS film coated on 400m long rolls of polyester substrate. The original pristine state of the polymer is almost transparent, with a light blue color. Further oxidation of the pristine semi-oxidized polymer makes it slightly more transparent, even though this change is hardly detectable by the human eye and, thus, not a very useful electrochromic effect. Reduction of pristine PEDOT:PSS toward the neutral state decreases the number of bi-polaronic states within the band gap and the optical absorption spectrum is shifted from the near infrared region into the visible region, peaking at approximately 640nm. This is a clearly visible electrochromic effect that results in a dark blue color, see the optical absorption characteristics of PEDOT:PSS in Figure 15.
Figure 15. Data, recorded by Payman Tehrani, of the optical absorption of PEDOT:PSS that shows the electrochromic property. The polymer becomes slightly more transparent upon further oxidation from the pristine semi-oxidized state, while the useful electrochromic switch occurs between the pristine (or oxidized) and the reduced states. The absorption maximum is shifted between the visible region, peaking at 640nm, and the near-infrared region in the reduced and oxidized state, respectively, and can be understood as the result of the significant increase in bi-polaronic states in the oxidized material.

3.2 The electrochromic display cell

The electrochromic display cell uses the change in optical absorption shown in Figure 15 and can be made in either a lateral or a vertical architecture. A lateral electrochromic display cell consists of two adjacent PEDOT:PSS electrodes with a patterned electrolyte layer between them that ensures ionic contact. Once a potential is applied between the electrodes, current can flow in a direction that depends on the polarity of the electrode potentials. The interface between the electrolyte layer and the polymer layer serves as a transducer that switches the current between electronic and ionic. One of the polymer electrodes is chosen to be the pixel, while the other acts as the counter electrode in the electrochromic display cell. The electrochemical reaction that occurs when a voltage is applied between the two electrodes causes the positively addressed electrode to become oxidized, while the negatively biased electrode becomes reduced, according to the electrochemical half-reaction

$$\text{PEDOT}^{+}\text{PSS}^- + \text{M}^+ + e^- \leftrightarrow \text{PEDOT}^0 + \text{M}^+\text{PSS}^-$$  \hspace{1cm} (1)
One advantage of using the same material in both electrodes, PEDOT:PSS in this case, is that it ensures low-voltage operation (below 2V). Equation (1) is written as a reduction, which is clearly observed as a switch of PEDOT into a semiconducting and deep blue colored state. Oxidation occurs if the half-reaction in Equation (1) proceeds from right to left, which results in higher conductivity and a transition towards transparency. Upon oxidation, the charge of PEDOT$^+$ is balanced by the polyanion PSS$^-$ and the electron e$^-$ and the cation M$^+$ are given up to the polymer film (and eventually the electronic circuit) and the electrolyte, respectively. Meanwhile, a reduction process occurs at the other electrode to maintain overall charge neutrality, which requires an electron for the conversion of PEDOT$^+$ to PEDOT$^0$, and the PSS$^-$ polyanion binds to a cation M$^+$ provided by the electrolyte instead.

Figure 16a shows the architecture of a lateral electrochromic display cell together with the migration of electrons and ions due to an applied electric potential. This electrochemical process is reversible and the pixel electrode can be cycled between the oxidized, transparent state and the reduced, deep blue colored state. However, if the process is driven further, either by excessive potential or a potential applied during a long time, the over-oxidized and irreversible state of PEDOT:PSS can be reached, effectively killing the device. Even though over-oxidation is detrimental to electrochemical devices, it can be used as an irreversible patterning method that separates conducting PEDOT:PSS areas in a polymer film by lines consisting of the non-conducting, over-oxidized state of PEDOT:PSS [33].
Figure 16. a) The lateral architecture of an electrochromic display cell is shown, including the migration of electrons and ions that are involved in the electrochemical reaction that occurs when a voltage is applied between the electrodes. b) The pristine, almost transparent, state and the reduced dark blue state of PEDOT:PSS are shown. These display cells are vertical and the counter electrode is hidden beneath a light gray-colored electrolyte.

Figure 16b shows the colors of oxidized and reduced PEDOT:PSS in a vertical display cell. This architecture is preferable over the lateral structure since the counter electrode can be hidden beneath the electrolyte layer, which in this case is light gray in color. Hiding the counter electrode dramatically increases the fill factor when the pixels are arranged into an active-matrix display. Furthermore, since the ion transport is the limiting process in devices that utilize a solidified electrolyte, the time required to switch the pixel electrode is lower in a vertical display because the distance the ions must travel between the two electrodes is at least an order of magnitude lower than the same distance in a lateral display, and the reduction occurs homogenously in the pixel instead of a reduction front that propagates in the lateral display cell architecture. The display cell architecture is bi-stable, which means that, once updated, the pixel electrode remains in the reduced state when the electric contacts are disconnected. This can be considered as a memory effect, and retention times ranging from a few minutes to many hours has been observed in display cells based on PEDOT:PSS.

There is, of course, a desire to obtain higher optical contrast and make colors other than the transparent versus dark blue available in PEDOT:PSS in electrochromic display cells.
Interested readers can find more information on the topic of additional colors and improved contrast in the work by Payman Tehrani et al. [34, 35], since only limited efforts have been spent on this in the thesis work presented here.

3.3 The electrochemical transistor

An electrochemical transistor device uses the electronic properties of PEDOT:PSS, that is, the conductivity of the polymer is switched when the material undergoes either electrochemical oxidation or reduction. Thus, the electrochemical transistor is a switchable device in which the impedance state of the PEDOT:PSS transistor channel controls the current through the channel. Two different architectures of the electrochemical transistor, that either contain three or four terminals, are briefly discussed below. A ratio of $10^5$ between the on-and off-currents in the transistor channel at an applied gate voltage of either 0V or 2V, respectively, has been observed and reported for the four-terminal device [16], while electrochemical logic circuits (inverters, oscillators, NAND- and NOR-gates) have been achieved using the three-terminal device [29].

3.3.1 Three-terminal electrochemical transistor device

A lateral three-terminal electrochemical transistor device consists of a stripe of PEDOT:PSS (the transistor channel) that, on either end, becomes the drain and source electrodes. The gate electrode (also PEDOT:PSS) is positioned adjacent to the channel. The transistor channel and the gate electrode are then ionically, but not electronically, connected by an electrolyte layer deposited on top of the PEDOT:PSS film, see Figure 17.
Figure 17. Lateral architecture of the electrochemical transistor consisting of the source and drain contacts on either side of the transistor channel. The gate electrode is ionically connected to, but electronically insulated from, the transistor channel by an electrolyte. The area of the electrolyte covering the gate electrode is typically at least 10 times larger than the area of the electrolyte defining the active area in the transistor channel. This allows for full depletion of the transistor channel upon reduction and minimizes the risk of over-oxidation of the gate electrode. Since PEDOT:PSS is electrically conducting in the pristine state, the resulting electrochemical transistor operates in depletion mode, that is, a gradual increase of the gate voltage gives a gradual switch towards the non-conducting state of the transistor channel.

The electrochemical reaction that occurs when a voltage is applied between the gate electrode and the transistor channel is still represented by Equation (1). This type of transistor operates in depletion mode since the PEDOT:PSS in the transistor channel is conducting in the initial state when the gate voltage is 0V, and the positive voltage that is applied to the gate electrode with respect to the transistor channel results in further oxidation of the gate electrode and, of more importance, reduction of the transistor channel. Therefore, depending on the value of the applied gate voltage, the conductivity of the transistor channel can be modulated between conducting and semiconducting. As can be seen in Figure 17, the area of the gate electrode is typically ten times larger than the active area of the transistor channel. The reason for this is that it ensures full depletion of the transistor channel from the semi-oxidized state of the gate electrode or, in other words, minimizes the off-current through the transistor channel.

The potential that drives the current through the transistor channel is applied between the drain and source contacts (V_{DS}), a potential that causes another electrochemical switching event to occur. The electrical resistance in the conducting state of the transistor channel is on the order of a few kΩ, resulting in a potential drop along the channel due to the applied V_{DS}. The active area of the transistor channel is defined by the area of PEDOT:PSS that is covered with an electrolyte layer and, hence, the positively addressed side of the active area in the
transistor channel will oxidize. The other side of the transistor channel undergoes a reductive electrochemical process due to the negatively applied bias voltage. The overall effect can be seen as a doping gradient within the transistor channel that pinches the transistor channel off, which in turn has been both observed in experiments and modeled as a steady-state current generator [36]. The pinch-off effect in combination with the gate voltage dependence is shown in the overall current versus voltage (I-V) characteristics in Figure 18.

![Figure 18. a) The I-V characteristics of the electrochemical transistor show two current regimes due to the pinch-off effect together with the gate voltage dependence. A pure resistive behavior is observed at low voltages, while the pinch-off gives rise to a saturated current regime at elevated voltages. Increasing the gate voltage from 0 to 2V results in a gradual decrease of the conductivity in the transistor channel. b) The same data as in a) in a semi-log plot. The current (density) level in the on-state ($V_G = 0V$) is about 250µA (250A/cm$^2$), while the current (density) level is around 50nA (50mA/cm$^2$) in the reduced off-state ($V_G = 2V$), and this results in an on/off-ratio of 5000.](image)

### 3.3.2 Four-terminal electrochemical transistor device

The idea of the four-terminal transistor device is the same as in the three-terminal device; to modulate the conductivity of the transistor channel by applying $V_G$ that allows for an electrochemical reaction to occur. However, the difference is that the gate has another electrode that is electronically connected to the transistor channel. Figure 19 shows the architecture of a lateral four-terminal electrochemical transistor device, including the T-shaped active area of the transistor channel. The four-terminal transistor architecture is operated with two different power supplies that are independent of each other, i.e. only connected through the transistor without a common ground, while the three-terminal device is operated with two different power supplies but the gate electrode is referenced to the source.
contact. The two electrochemical transistor architectures mentioned here will be further discussed in the following chapters.

Figure 19. The lateral four-terminal electrochemical transistor is shown. A negatively biased gate electrode that is electronically connected to the transistor channel is added, and the reduction appears in the shape of the letter T. The gate power supply, indicated with filled circles, is disconnected from the potential applied at the open circles between the source and drain electrodes.

### 3.4 Electrochemical smart pixels

The combination of an electrochemical transistor and an electrochromic display cell makes a smart pixel, which thus uses both the electronic and opto-electronic properties of the material. An active matrix addressed display can then be achieved by arranging the electrochemical smart pixels into a cross-point matrix. The electrochemical transistor allows the electrochromic display cells to be uniquely addressed since the applied gate voltage controls the current flow through the transistor channel, which results in minimized cross-talk in the matrix. A simple sketch of an electrochemical smart pixel circuit together with typical chronoamperometric response to changes in applied potentials are shown in Figure 20. In the experiment shown by the graph that displays the current behavior, $V_G$ and $V_{DS}$ were set to 0 and 2V, respectively, in the beginning of the measurement, leaving the transistor channel in its conducting state and allowing for the display cell to be updated to its blue-colored state. The charge loaded into the display cell during this update was determined to 0.46mC. $V_G$ was then set to 2V in order to switch the transistor channel to its non-conducting state. After a few seconds, $V_{DS}$ was set to 0V. The transistor channel was then switched to its conducting state again after five minutes, which enabled the display cell to discharge as indicated by the negative current. The total discharge was $-0.44mC$ in this case. The two narrow current peaks
at 27 and 338 seconds, respectively, are not included in the integration since they are believed to occur from discharging of the transistor channel and not from the display cell. The fact that the charge transported in both events is nearly identical, that is, the ratio of the two numbers equals 96.5%, indicates that the transistor is capable of retaining the information in an updated display cell.

3.5 Three- or four-terminal transistors in the smart pixels

A four-terminal electrochemical transistor was used in the matrix displays reported in Paper 1. Figure 3 in that paper clearly shows that the charges stored in the display cell are, to some extent, lost after only 55 seconds. Comparing this with the graph in Figure 20 above
indicates that the three-terminal transistor should be used since this device shows very small off-current, typically below 100nA, 50nA in Figure 18, which is an advantage when charges are to be retained in a smart pixel. The observations from the characterization of smart pixels based on four-terminal transistors presented in Paper 2 also resulted in higher off-current. Furthermore, the high retention ratio of 96.5%, as calculated earlier for the three-terminal transistor, is probably due to the gate current contribution to the display cell in the off-state, an effect that cannot occur in the four-terminal transistor since the applied voltages are disconnected to each other. Notice that different electrolytes, as well as different geometries and device dimensions, have been used in Paper 1, Paper 2 and in the work with the three-terminal transistor reported in this thesis, which complicates analysis and conclusions.

However, from a manufacturing point of view it is clear that the three-terminal transistor device should be used. The four-terminal transistor used in Paper 1 required an additional resistor on the negatively biased gate electrode in each transistor in order to reduce cross-talk when the smart pixels were arranged into cross-point matrices. Furthermore, the conducting lines of that particular system had to be crossed by the use of electrical vias. Each of these add extra patterning steps to the printing process. Thus, there is a significant advantage to using the three-terminal electrochemical transistor in the electrochemical smart pixel device - manufacture in a printing process requires only four steps - resulting in a straightforward layout of the smart pixels into an active-matrix display. Even though both the electrochromic display cell and the electrochemical transistor were presented as lateral devices previously, they are preferably manufactured in a vertical architecture in active-matrix displays in order to increase the fill factor, i.e., the ratio of the pixel electrode area to the total area of each electrochemical smart pixel. Another advantage with the vertical design is that the response to electrochemical switching occurs more quickly since no lateral propagation of the reduction front is required, especially important in display cells that have an area of 1cm$^2$ or greater.

### 3.6 Electrolyte dependence

The electrolyte layer that is required for the electrochemical switching process needs to be confined to specific areas. This is especially important in the electrochemical smart pixel device and in the active-matrix display since the two electrolytes used in the transistor and the display cell must remain physically separated in order to prevent leakage currents and unexpected electrochemical reactions. This can, for example, be achieved in a patterning step
similar to screen printing, in which the electrolyte layers are defined through a plastic mask. Various aqueous electrolytes have been used in the manufacturing of active-matrix displays, partly because they are easily processed and partly because they can be transformed into solidified electrolyte layers after the printing step by evaporating the water at elevated temperature. Various concentrations of liquid electrolytes based on sodium sulfate, Na$_2$SO$_4$, were used in the electrochemical smart pixel characterization presented in Paper 2. The main conclusion drawn from those experiments was that high ionic conductivity, i.e. a high salt concentration of 1M Na$_2$SO$_4$ in a liquid electrolyte, of the electrolyte resulted in a smaller off-current through the transistor channel compared to electrolytes with lower (1mM Na$_2$SO$_4$ salt concentration) ionic conductivities; an effect that is believed to arise due to a deeper reduction in the transistor channel obtained with increased salt concentration. This was also, to some extent, verified by the time response of the transistor, where an electrolyte with high ionic conductivity resulted in faster turn-off but slower turn-on compared to the case with low salt concentration. Ideally, the turn-on response of the transistor would also be increased with increasing concentration, but a deeper reduction state causes a decreased conductivity of the PEDOT, which in turn results in a slow time response.
4 Active matrix addressed displays

There are a large number of electronic devices in which the displays are updated with direct addressing [37] on the market today; familiar examples include liquid crystal displays in calculators and digital watches. Such displays typically consist of a certain number of seven-segment characters that have been defined during the manufacturing process. In order to present more complex information on a display, such as graphics, a technique like matrix addressing has to be used. The general idea behind matrix addressing is that the display cells are arranged in rows and columns to form a matrix, which can be updated row by row. Each section of the entire display can then be uniquely addressed by applying the updating potentials in a proper way. The number of electronic connections required in matrix addressing is then (rows + columns), instead of (rows \times columns) in a non-matrix addressed display, which becomes very important in displays that contain a large number of pixels [38]. The problem with cross-talk might occur in passive matrix addressed displays, since the applied voltage cannot update one unique display cell in the matrix without affecting other display cells, resulting in reduced contrast when the number of rows is increased. An actively addressed matrix display [39], where a switchable transistor device is connected to each display cell in a smart pixel, circumvents this problem. The transistor in the smart pixel is the “active” part since it controls the current to and from the display cell in the matrix.

As previously discussed in the electrochemical smart pixel chapter, the three-terminal electrochemical transistor has an outstanding advantage over the four-terminal transistor from the manufacturing point of view since no resistors or electrical vias are required. The architecture of a 2\times2 active-matrix display is shown in Figure 21. The requirement for the resistors when the four-terminal transistors are used in matrices is further discussed in Paper 1, and Figure 2 in that paper clearly shows the need for electrical vias when the conducting lines are crossed.
Figure 21. Smart pixels arranged into a 2x2 active-matrix display. a) The lower layer of the display consists of column lines, the transistor channel and the counter electrode, all patterned in PEDOT:PSS and indicated by a gray color. An electrolyte layer, indicated in black, is then patterned and defines the active region of the transistor channel and the counter electrode. b) The upper layer consists of the row lines for the transistor gate electrodes as well as the lines connecting the pixel electrodes and the pixel electrodes themselves, all patterned in PEDOT:PSS and indicated in gray. As the fourth printing step, the electrolyte layer indicated in black defines the active region of the gate electrode and the active pixel area. c) A lamination process brings the two layers into ionic contact. This will eventually require an additional plastic layer to prevent electronic short-circuits between the PEDOT:PSS in the two layers. A total of only five steps is required to complete the matrix display.

The 2x2 active-matrix display layout shown in Figure 21 is applicable for an arbitrary number of rows and columns. The electrochemical transistors in the resulting matrix display are updated row by row, while the electrochromic display cells are updated column by column. By keeping the transistors in row 1 conducting, while an applied gate voltage forces the rest of the transistors in the remaining rows to their non-conducting state, the display cells in row 1 can be updated by the appropriate voltage at each column. The gate voltage is then applied to row 1 and the process repeated for row 2. This procedure is repeated until the full matrix
display has been updated. The role of the electrochemical transistor is two-fold. First, the transistor retains charges inside an updated display cell and, second, the transistor minimizes cross-talk within each column of display cells. The fulfillment of these criteria allows for unique addressing of each display cell in the active-matrix display, as is demonstrated in Figure 22.

Figure 22. a) The experimental updating procedure of a 3x3 active-matrix display printed from all-organic materials. The images are arranged (0 to 5) according to the update sequence in the b) figure. b) The applied potentials during an update cycle of the matrix display are shown. (0): The display is initially blank. (1): Gate voltages are applied to row 2 and 3, while the transistors in row 1 are kept conducting, and the display cell voltage in the left column line is addressed in order to color the upper pixel to the left. If it were not for the non-conducting transistors in row 2 and 3, the column potential would color all pixels in the left column. (2) The transistors in row 1 are switched to the non-conducting states, while they instead are switched to the conducting states in row 2. The transistor that belongs to the updated pixel in row 1 retains the charges inside this pixel. A potential is applied to the column addressing lines to the left and in the middle and the corresponding pixels in row 2 are updated. (3) The same updating procedure is successively carried out throughout the remaining rows in the display, i.e. only row 3 in this particular display. (4) All transistors are in their non-conducting state and the information can be stored in the matrix display, even though a potential of 0V is applied to the column addressing lines. (5) The information in the display is discharged by an intended short-circuit that allows charge migration to the initial equilibrium state.
The area of the gate electrode is typically ten times larger than the area of the active region in the transistor channel in order to minimize the risk of over-oxidation and to fully deplete the channel and, hence, achieve the maximum current modulation [40]. This is not a major problem from a fill factor point of view since the channel is relatively small compared to the pixel electrode, typically on the order of 1mm$^2$ compared to 1cm$^2$, respectively. However, the latter requires a counter electrode sufficiently large in order to achieve good contrast within the pixel, which is a complication in a matrix display where a high fill factor is desired. A vertical design increases the fill factor drastically compared to the lateral architecture, but is still insufficient. To further increase the fill factor, the area of the counter electrode can be decreased while holding the volume of the electrode constant if an extra layer of PEDOT:PSS is added, which has an immediate impact on the fill factor. As long as the counter electrode layer is sufficiently thick for the pixel electrode to be fully reduced, the highest available contrast will be reached. Switching will occur most quickly in the part of the pixel electrode area that is located directly above the counter electrode since the ion transport is the limiting process. However, switching will be significantly slower for the remainder of the pixel electrode, as the colored region spreads laterally away from the counter electrode, as observed by the eye as a blue colored front propagating towards the edge of the pixel electrode. Hence, there is a trade-off between switching speed and fill factor due to the combination of vertical and lateral electrochemical switching of the display cell. The switch speed for various area ratios between the counter and pixel electrodes are shown in Figure 23.
Figure 23. All display cells presented in this figure are stacked in a vertical architecture. The graph indicated with squares represents an ordinary display cell where the counter and pixel electrodes are equal in size. It is switched from transparent to dark blue in about five seconds. The other three graphs represent display cells with an additional layer of PEDOT:PSS on the counter electrode to ensure maximum reduction of the pixel electrode, where the counter electrode area is 100%, 50% or 10% compared to a fixed pixel electrode area in the graphs indicated with circles, triangles and stars, respectively. The initial current levels when the additional layer of PEDOT:PSS is used are about one order of magnitude higher compared to the display cell without the extra layer. A counter/pixel electrode area ratio of either 100% or 50% ensures that the pixel electrode switches faster than the original display cell. The time response in the graph with stars, where the counter electrode covers only 10% of the pixel electrode area, seems to occur very fast, but that is only the vertical switching that colors 10% of the pixel. The vertical switching then changes to lateral, as seen by the eye and understood by the high current after ten seconds, which effectively means that the pixel electrode still contains regions of highly conducting PEDOT:PSS.

The fill factor was approximately 29% in the matrix displays reported in Paper 1. The design used at present day has resulted in 8×8 active-matrix addressed displays with a fill factor of 42%, where the improved fill factor mainly is attributed to the use of the three-terminal transistor. However, a decrease in the counter electrode area by the usage of an additional layer of PEDOT:PSS has an impact on the design of the electrochemical smart pixel, and the fill factor is predicted to increase to at least 64% while maintaining color contrast in the display cell, see Figure 24. Unfortunately, no experimental data are available with this design yet.
Figure 24. a) The left panel shows the current smart pixel design that results in a fill factor of 42%, an improvement over the fill factor of 29% reported earlier in Paper 1. The right panel shows how the counter electrode area can be reduced in size, as long as an additional layer of PEDOT:PSS on top of the counter electrode provides full reduction, and hence, full blue coloring, of the pixel electrode. The counter electrode is 76.5% of the pixel electrode in this particular figure, and that should give a smart pixel fill factor of 64%. b) Simplified schematics of three 3×3-matrices that show the impact of higher fill factor.

The matrix displays that have been manufactured within this project utilize only organic materials. Specifically, this means that PEDOT:PSS has been used as the active switch material in electrochemical transistors, the electrochromic material that changes color in the display cells and the material that serves as the conducting lines in every row and column of a matrix. A potential drop occurs along the conducting lines since the Orgacon foil has a sheet resistance of about $300 \Omega/\square$, which in turn yields lower updating potentials in display cells that are located in the lower rows of the matrix display and, hence, slower switching events.

The most significant disadvantage of this system is the combination of the depletion mode transistor and the ionic conductivity in PEDOT:PSS since this is detrimental to the time response of the transistor channel. One reason for the slow response when the transistor channel is switched from non-conducting to conducting was touched upon earlier (and further discussed in Paper 2), with the conclusion that a deep reduction slows down the transistor. However, this effect is believed to be valid only for short time scales, i.e. here in the order of several seconds, while another phenomenon denoted the propagating front [41] overrides the short time effect on a longer time scale, typically above ten seconds. The propagating front occurs because PEDOT:PSS conducts ions, which results in a reduction front beyond the electrolyte edge in the transistor channel due to the applied voltage between the drain and source electrodes. This reduction front propagates through the polymer film on the millimeter scale, also for voltages as low as 2V, and can clearly be observed by the human eye as a moving blue package. Transistors used in active-matrix displays are, due to the updating
technique, switched to their non-conducting state according to a ratio equal to $\frac{n-1}{n}$ of the total time required for the updating sequence, where $n$ is the number of rows in the matrix. This means that each transistor device is reduced most of the time and withstands the applied potential from the column addressing line in order to minimize cross-talk. This puts a lot of strain on each transistor every time the corresponding column line is addressed, which in turn might force the reduction package to propagate outside the electrolyte edge. In addition to this, we are not able to actively bias the gate voltage with reverse polarity due to the risk of over-oxidation of the PEDOT:PSS in the transistor channel. A switch towards the highly conducting state can only be achieved from a discharge of the propagated reduction front outside the electrolyte edge in the transistor channel by applying $V_G = 0V$. This is a very time consuming operation that occurs in each extra row that is added to a matrix display. The 8×8 active matrix addressed display reported on in Figure 25 showed an updating response time ranging from seconds for the first row to several minutes for the last row.
Figure 25. a) The left panel shows an 8x8 active-matrix display updated as a chessboard with a fill factor of 42%. To demonstrate reversibility, the inverse arrangement of a chessboard was updated in the same matrix display, shown in the right panel. The display cell in row 3, column 5 was, for an unknown reason, malfunctioning in this particular matrix display. The contrast is significantly less in this prototype than in other demonstrators because a transparent electrolyte layer was used. b) This image shows a 4x8-matrix display, also switched to show the pattern of a chessboard, with improved contrast due to a light gray opaque electrolyte layer. c) A picture that shows the flexibility and bi-stability of the matrix display. All external electronics have been disconnected but the image still remains.
Figure 25 shows a few of the actively addressed matrix displays that have been manufactured by using the three-terminal electrochemical transistor device. The manufacturing process is very straightforward, as briefly discussed in the caption to Figure 21. The layout of the devices in the matrix displays was created by subtractive patterning of the homogenous PEDOT:PSS layer on the Orgacon foil. Each one of the two layers was patterned in this fashion. One electrolyte layer for each pre-patterned Orgacon foil was then deposited through holes in a plastic mask. Apart from the confinement of the electrolyte layers, the plastic masks also prevent short-circuits between the conducting PEDOT:PSS layers when they are laminated together in the final matrix display. Making the disposable plastic masks is, unfortunately, the most time-consuming step in the hand-craft manufacturing process with an approximate requirement of four hours for a display that consists of 8×8 smart pixels. Furthermore, experience from the laboratory has shown that the manufacturing time scales linearly with the total number of smart pixels, which may explain why this project has been limited to matrix displays that contain rather few smart pixels.

Despite the challenges, the concept of active-matrix displays based on electrochemical smart pixels printed on flexible substrates has been proven. Random patterns of information can be presented on displays manufactured with this technique.
5 Optical polarizer based on electrochromic switching in stretch-aligned polyaniline

This project deviates a bit from the active-matrix display concept previously discussed. It is based on the combination of electrochromism and optical polarizing effects in stretch-aligned conjugated polymer chains, and is further discussed in Paper 3.

Increasing the dichroic ratio, that is, the orthogonal transmitted intensity divided by the parallel transmitted intensity, through the orientation of conjugated polymer chains has been demonstrated in the past [42, 43]. Such chain orientation results in devices that exhibit polarized opto-electronic and electronic characteristics [44-47]. Another approach to changing both the optical and the electrical properties of a conjugated polymer is to utilize an electrochromic polymer in a lateral display cell setup as described previously. The switchable optical polarizer is a result based on the combination of electrochromism and stretch-alignment. Polyaniline, whose oxidation states were shown in Figure 12, was chosen as the electrochromic material. The initial highly conducting form of polyaniline is known as the dark green colored emeraldine state. The polymer switches to the electrically insulating leucoemeraldine state upon reduction, which shows a pale yellow color. The electrically semiconducting pernigraniline state, obtained through oxidation of the polymer, is dark blue to its color.

A simple device was manufactured with a vertical architecture consisting of a thin foil of polyethylene serving as the carrying substrate, a spin-coated layer of poly(methyl methacrylate) providing for better adhesion to the next layer, which is a spin-coated active layer of conducting PANI. The resulting film was then stretched to an elongation factor of between 5 and 10 at elevated temperature. The stretch-alignment results in a higher degree of orientation of the PANI chains, which in turn yields optical polarization. Two adjacent layers of electrolyte were then deposited on top of the stretched film and a potential of a few Volts can be applied. This will switch the positively biased part of the film to the oxidized pernigraniline state, while the negatively addressed part switches to the reduced leucoemeraldine state. The optical polarization property of this device was determined by the use of an optical absorption spectrometer in combination with an ordinary polarizer to limit the orientation of the incoming light. The peaks in absorbance, in both oxidation states, differ
depending on if the incoming light is polarized parallel or orthogonal to the orientation of the stretch-aligned PANI chains.

Figure 26a shows how vertical stacking of two of these devices, oriented orthogonally to each other, results in the switchable optical polarizer. As explained in the caption for Figure 26b, the orientation of the resulting polarized absorption can be reversibly switched (through the polarity of the applied voltage) between two different directions that depend on the oxidation state of the respective polymer layer.

Figure 26. a) The architecture of the switchable optical polarizer is shown. b) This figure shows the polarized transmitted intensity versus the polarization direction of the incoming light of the switchable electrochromic polarizer measured with a photo diode. In the graph indicated with squares, the stretch-aligned polymer chains in the PANI film switched to the pernigraniline state were oriented in parallel with the initial polarization direction of the incoming light. In the graph marked with circles, the pernigraniline polymer chains were orthogonally oriented to the initial polarization direction of the incoming light, resulting in a higher degree of transmittance. Copyright 2003, American Institute of Physics.

The idea of combining electrochromism and the optical polarizing effect achieved through stretch-alignment of polymer chains is a novel phenomenon in itself. Utilizing this effect as an active device in order to enhance the contrast in electrochromic display cells, or in other display applications, similar to the two passive polarizers that are used in twisted nematic liquid crystal displays [45] were also considered. However, complex manufacturing in combination with low dichroic ratios that do not cover the full visible wavelength region terminated this project after the publication of Paper 3.
6 Conclusions and outlook for the future

The contributions presented in this thesis have established a rather straightforward process for manufacturing active matrix addressed displays based on electrochemical smart pixels printed on flexible substrates. Even though this technology cannot compete with other display technologies in terms of speed, it shows several other strong advantages:

- Low voltage operation makes direct incorporation of printable batteries in the matrix displays possible.
- Soluble, all-organic materials allow flexible matrix displays to be manufactured on either paper or plastic substrates
- The electronic property of PEDOT:PSS is used in both the electrochemical transistors and in the conducting lines, while the opto-electronic property is used in the electrochromic display cells. Thus, only one active material is required in the matrix displays.
- The three-terminal electrochemical transistor could possibly enable reel-to-reel manufacturing of matrix displays since neither additional resistors nor electrical vias are required, simplifying the display design considerably.

Based on this, I see no particular reason in continuing this project through hand-craft, but it would be an interesting challenge to establish a manufacturing process for the active-matrix display concept in a joint collaboration with the Acreo research institute using the Nilpeter Rotolabel FA3300/5 printing press, see Figure 27, located in our common research facility in Norrköping.

In addition to this, a manuscript is in progress regarding recent ideas and experiments on the topic of active-matrix displays. Some of the results that belong to that manuscript have been discussed and presented in this thesis since a full manuscript was not available at the time of press. This manuscript should, in its final version, contain a section on active matrix addressed display modeling carried out by Associate Professor Robert Forchheimer, Department of Electrical Engineering, Linköping University, and will hopefully be submitted to a refereed journal during the spring of 2006.
When that has been accomplished, I will step with my other foot in a leap towards the understanding of switchable molecules in polymer diodes, an attempt that hopefully will give me the opportunity to stand here in the very same spot in about one year with both feet on the ground.

Figure 27. The Nilpeter Rotolabel FA3300/5 printing press that is located in our research facility. The operating personnel at the Acreo research institute are at the moment developing a process for printed electrochromic displays in the machine. Copyright: Niclas Kindahl, Fotofabriken.
7 References


Paper 1

Active Matrix Displays Based on All-Organic Electrochemical Smart Pixels Printed on Paper

Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren

Organic Electrochemical Smart Pixels

Peter Andersson, David Nilsson, Per-Olof Svensson, Miaoxiang Chen, Anna Malmström, Tommi Remonen, Thomas Kugler and Magnus Berggren

Paper 3

A Switchable Optical Polarizer Based on Electrochromism in Stretch-Aligned Polyaniline

Peter Andersson, Thomas Kugler and Magnus Berggren